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SOLID-PHASE SYNTHESIS AND SINTERING IN HIGHLY DISPERSE OXIDE-METAL POWDER MIXTURES

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The specifics of using ultrafine electroexplosive metal powders in powder metallurgy and ceramic technology are considered. The possibility of activating the processes of sintering and synthesis of certain complex oxides and silicates is demonstrated. The effect of metallic additives on hardness, strength, and other properties of materials is established. Reinforced powdered and solid composites are produced in the combustion of oxide-metal mixtures.

The obvious advantages and prospects of highly disperse materials for ceramic production are discussed in many publications [1]. A great part of them currently concentrate on studying nanodisperse (cluster less than 10 nm) powders produced by different methods and articles based on these powders [2, 3]. There are significantly fewer studies of the possibilities of coarser and technologically more effective powders [4] obtained by electric explosion of conductors (EEC) [5]. These materials are more frequently classified as superfine or ultradisperse powders, and their particle size ranges from 0.03 to 0.10 μm . The studies carried out at the Silicate Technology Department of Tomsk Polytechnic University and at the Research Institute of High Voltage demonstrated the promise of using these powders for a whole spectrum of functional materials: disperse-strengthened metals, antifriction and superhard materials, intermetallic, heat- and electroconducting materials, dielectrics, etc.

The present study considers some specifics of behavior of electroexplosive superfine powders (SFP) in the heat treatment of metallic and oxide-metal mixtures and possibilities of producing intermetallic, metal-ceramic, and ceramic-metal composites.

The EEC method is used to obtain superfine powders of aluminum, iron, copper, nickel, titanium, tungsten, silver, and some other metals, as well as their oxides, carbides, and nitrides (Research Institute of High Voltage, Tomsk). One should note the substantial energy-saturation of such powders [6, 7] and at the same time their sufficient resistance to oxidation in normal conditions under high dispersion (specific surface area of 5 – 20 m^2/g). Figure 1 shows the heating curves of ultradisperse copper powder in a nitrogen medium that clearly illustrate the emission of excessive energy. The exothermic effect correlating to this process (570°C) is

not accompanied by a change in the powder weight and is equal to 16.7 kJ/mole. The accumulated energy of some metals after pulse spraying of conductors and stabilization of SFP is equal to 10 – 60 kJ/mole [6]. These properties contribute to a rapid expansion of application areas of electroexplosive powders. They are promising for ceramic technology [8] and for powder metallurgy.

Electroexplosive metallic SFP in heating (400 – 600°C) react chemically and by diffusion virtually with all known materials, including inert and low-activity ones, such as Pt or Al_2O_3 . The unique reaction capacity of SFP, which is related to the dimensional factor as well as to the state of the structure, is used in various processes, including solid-phase processes.

Studies demonstrate that metallic SFP under thermal treatment can easily form intermetallic compounds and solid solutions at lower temperatures and at a higher rate. Energy-saturated powders of pure metals sinter in a regime resem-

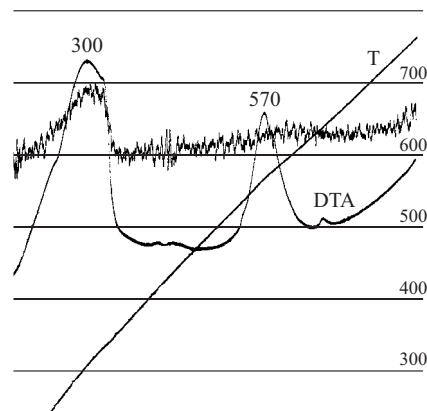


Fig. 1. Thermogram of ultradisperse electroexplosive copper powder in nitrogen medium.

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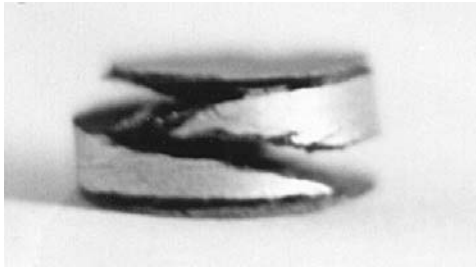


Fig. 2. A sample made of aluminum SFP sintered with self-heating.

bling self-propagating high-temperature synthesis (SHS). Figure 2 shows a sample made of pure electroexplosive aluminum that was sintered in vacuum on a belt heater heated from beneath up to 250°C. The sintering lasted 1.5 sec. The sintering front has passed via the sample in the form of a luminescent spiral-shaped wave; therefore the sample exhibits spiral stratification.

In the course of sintering composites containing ultra-disperse copper and aluminum, iron and aluminum, iron and nickel, and even such seemingly incompatible metals as high-melting tungsten and aluminum using electroexplosive SFP, disperse-strengthened intermetallics and oxides were identified. Thus, as a consequence of x-ray photoelectron spectroscopy, compounds of the type WAl_4 and WAl_2 were registered after sintering in the W – Al system. Abnormally high microhardness values of the sintered composites (Fig. 3) were registered with the atomic ratio W : Al equal to 5 : 1, 1 : 1, 1 : 2, and 1 : 20.

The reaction capacity of superfine metallic powders can be used in the production and strengthening of metal – metal, metal – glass, and ceramic – metal soldered composites to replace low-melting transitional glasses [9]. Thus, a composite containing finely disperse powders of tungsten ($d_{av} = 0.3 - 0.4 \mu m$), copper ($d_{av} = 0.1 \mu m$), and aluminum ($d_{av} = 0.12 \mu m$) together with coarse industrially produced tungsten and molybdenum powders ($d_{av} = 5 - 40 \mu m$) was tested in attaching quartz to tungsten in making current inputs for gas-discharge bulbs. The component that ensures improved adhesion in this case is not only the SFP of relatively low-melting copper but finely dispersed tungsten as well, which already at 1000°C actively adheres to the bulk metal.

Electroexplosive ultradisperse powders can be successfully used to solve such problems of powder metallurgy as increasing hardness and strength of sintered articles made of stainless steel, as well as recycling grinding and cutting waste of expensive alloys. For instance, the hardness of alloy based on steel ShKh15 is only 30 – 36 HRC and its bending strength 170 – 190 MPa. The use of a small amount of ultra-disperse electroexplosive iron powder ($d_{av} = 0.2 \mu m$) makes it possible to raise the hardness of this alloy, including as well the method of adding hard minerals such as corundum or quartz without impairing the mechanical strength of the sintered sample. The effect of STP – Fe additives on the

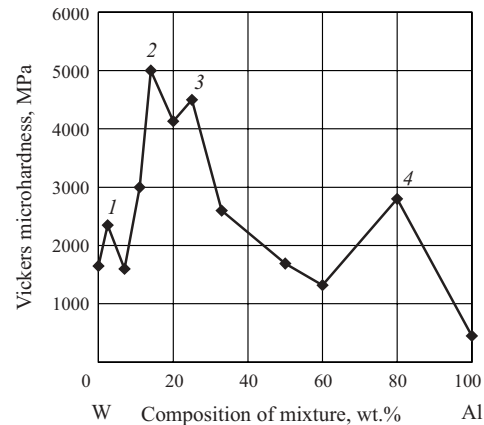


Fig. 3. Microhardness of sintered tungsten-aluminum powder composites. Atomic ratio W : Al = 5 : 1 (1), 1 : 1 (2), 1 : 2 (3), and 1 : 20 (4).

properties of dispersion-strengthened powder alloys is shown in Table 1. The average diameter of sintered steel powder particle was 25 μm , and that of introduced oxides was 6 – 10 μm .

As the material sinters, a small quantity of mullite $Al_6Si_2O_{13}$ is formed, which additionally increases its hardness. However, the introduction of oxides in this case does not increase the brittleness of the material due to the sintering effect of ultradisperse iron. This is manifested in the increasing strength of contact between the steel particles and in the formation of transitional reaction zones in the form of the fayalite phase on the surface of the quartz grains. The emerging dispersion-strengthened alloy is a finely crystalline structure with a homogenous distribution of oxide and metallic components. Furthermore, the introduction of ultra-disperse metal makes it possible to decrease the sintering temperature.

In utilization of grinding waste, ceramic (containing abrasive waste of Al_2O_3 and SiC), ceramic-metal (WC – Co), and purely metallic materials with satisfactory properties were synthesized using SFP of iron, copper, and nickel. The introduction of electroexplosive nickel powder ($d_{av} = 0.15 \mu m$) is especially effective for sintering cutting-tool powders, including those obtained by separation of slime waste. The use of this powder allows for additional dis-

TABLE 1

Sample	Mixture composition, wt.%*		Sintering temperature, °C	Hardness, HRC	Bending strength, MPa
	ShKh15	Fe _{SFP}			
1	67.0	0	1250	34	180
2	66.8	0.2	1250	37	190
3	66.6	0.4	1200	46	230
4	66.5	0.5	1200	48	255
5	66.4	0.6	1200	50	240

* In all cases SiO_2 content was 8.0% and Al_2O_3 content 25.0%.

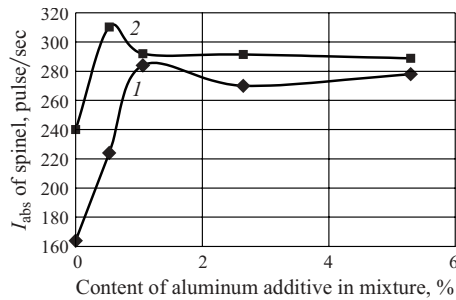


Fig. 4. The effect of ultradisperse aluminum additive on the synthesis of aluminomagnesium spinel at 1200°C (1) and 1250°C (2): I_{abs}) absolute intensity of x-ray maximum of spinel ($d = 0.285$ nm).

persion strengthening of sintered materials using oxide powders such as silicon and aluminum oxides and aluminomagnesium spinel without a loss in mechanical strength (Table 2).

A small quantity of metallic SFP (in this example from 0.4 to 2.0%) is sufficient to attain the strengthening effect. Although electroexplosive powders are inferior to nanopowders obtained by other methods (plasma-chemical, etc.) in dispersion, they are no less active and, which is very important, more convenient to use. They are less aggregated and their agglomerate sizes are smaller by an order of magnitude than those of plasma-chemical powders. They have virtually no hollow particles. When produced in the special explosion chamber, electroexplosive SFP particles are coated in a gaseous cover and have a double electron layer, which in passivation becomes chemically stabilized and has high pseudocapacity [6]. In contrast to colloid particles, electroexplosive particles are hard to polarize and have a total charge approaching zero. All this facilitates homogeneous distribution of superfine powder particles over the matrix of coarse industrial powders with formation of their own layer not more than 0.7 μm . When heated to 250 – 400°C (depending on the chemical type), metallic SFP rapidly enter in reactions with oxides or with the ambient medium and have virtually no melted yield of their own.

Based on the performed studies, it is possible to trace several directions in ceramics technology, in which the use of electroexplosive powder appears promising:

- activation of ceramic mixture sintering;
- activation of solid-phase synthesis processes;

TABLE 2

Sample	Mixture composition, wt.%			Microhardness, MPa
	cutting material waste	nickel SFP	MgAl_2O_4	
1	100	0	0	1887
2	98	2	0	2318
3	93	2	5	2867
4	88	2	10	4983
5	83	2	15	4872
6	78	2	20	3022

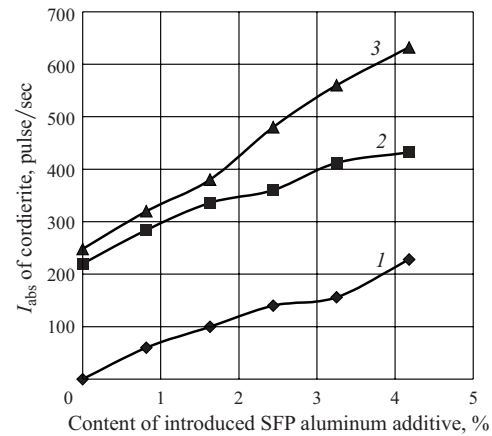


Fig. 5. The effect of SFP aluminum additive on the synthesis of cordierite in a mixture of natural silicates at 1150 (1), 1200 (2), and 1250°C (3): I_{abs}) absolute intensity of x-ray reflection of cordierite ($d = 0.854$ nm).

– modification of the structure of ceramic materials, including production and stabilization of certain polymorphic forms;

- SHS process;
- synthesis of ceramic mixture components in combustion;
- production of ceramic – metal and metal – ceramic composites in a reducing medium and by hot molding.

The activating effect of additives such as Cu, Ni, Al, and Al_2O_3 – Al composites obtained also by the EEC method is manifested primarily in the sintering of high-melting oxides: Al_2O_3 and ZrO_2 . The materials sharply differ in their physicochemical parameters depending on the sintering conditions, the main of which is the firing medium. Sintering of Al_2O_3 and ZrO_2 with SFP metal additives in an oxidizing atmosphere results in the nearly total transformation of metals into oxides. Furthermore, with a corresponding selection of mixture components and a high density of molded samples, metallic SFP enter into chemical reactions with the matrix oxides.

It was found in experiments in solid-phase synthesis of complex compounds that aluminum SFP forms a highly active ultradisperse oxide and, consequently, acts as the activator of synthesis of complex compounds (Figs. 4 and 5). Multiple experiments in different furnaces demonstrated that the necessary condition is a sufficient content of oxygen in the furnace atmosphere. A decrease in the partial pressure of oxygen to 0.103×10^5 Pa virtually completely stops the process. Consequently, the metal (Al) in synthesis first has to pass via the oxidation stage and only afterwards or, possibly simultaneously, does the metal in the form of ion occupy a position in the respective sublattice of the new compound, in our case, cordierite or aluminomagnesium spinel. The latter assumption of the highest activity of metal additives at the moment of their oxidation agrees with the fact that in the case of introducing an equivalent amount of ultradisperse

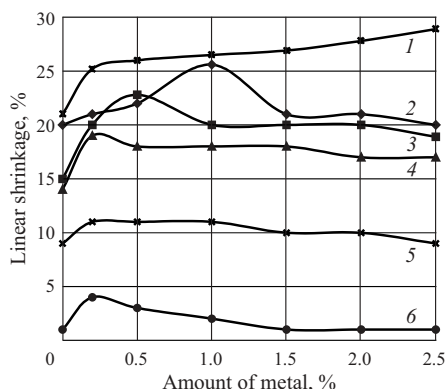


Fig. 6. Sinterability of composites with SFP metal additives: 1) $\text{Al}_2\text{O}_3 - \text{ZrO}_2$ with Ni additive; 2) $\text{ZrO}_2 - \text{Al}_2\text{O}_3 - \text{Y}_2\text{O}_3$ with Al additive; 3) $\text{ZrO}_2 - \text{Y}_2\text{O}_3$ with Al additive; 4) $\text{ZrO}_2 - \text{CaO}$ with Al additive; 5) ZrO_2 with Al additive; 6) Al_2O_3 with Ni additive; 1 – 4) composites based on plasma-chemical oxide powders; 5 and 6) vibration-milled oxides.

aluminum oxide, which is more disperse than the metal, the yield of the products of synthesis is lower.

The efficiency of synthesis and sintering of ceramics materials using SFP metals as activators depends as well on the dispersion of the matrix material. When ultradisperse metallic powder is introduced into the sintering system, the optimum amount of the additive slightly decreases with increasing size of the main oxide particle. If the sizes of the sintering oxide and the activator additive particles are comparable (for instance, powdered obtained by plasma-chemical synthesis and by the EEP method in sintering of aluminum oxide), the optimum weight content of the activator metal lies within the limits of 0.50 – 1.75% (Fig. 6, curves 1 – 4). When the activated process consists in sintering of a more coarsely disperse oxide (milled in a ball mill or a vibration mill), the optimum quantity of the additive does not exceed 0.25% (Fig. 6, curves 5 and 6).

This regularity is caused by the necessity of developing a thin transitional layer in the space between the grains of the sintering oxide, taking into account the geometric ratio of particles of heterogeneous materials. As the content of the metallic additive grows above the optimum value, the emerging transitional layer becomes excessively loose due to its own phase rearrangement, which has no time to be completed in the short sintering interval. The condensation effect in this case would be completely lost.

Rapid heating in vacuum or hot molding in a reducing medium, in contrast to the above described process, facilitates the preservation of the additive in its metallic form, and therefore the high activity of metallic SFP can be used also in the production of metal ceramics. In these processes it is advisable to use relatively inert metals (Cu, Ni, Ag), whose sintering role is based on the formation of liquid-phase interlayers with good adhesion to the sintering oxides (Al_2O_3 , ZrO_2 , etc.). Such chemically active additives as aluminum or titanium SFP are less effective in these firing conditions,

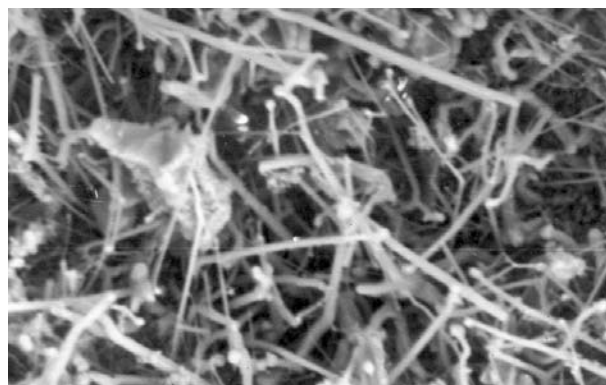


Fig. 7. Reinforcement of silicate matrix by aluminum oxide and nitride crystals.

since in the absence of a sufficient amount of oxygen, the reactions and the phase-stabilizing processes of newly formed oxides and compounds do not have time to take place during the short firing interval. The bending strength of such materials does not exceed 200 MPa. In contrast, aluminum and zirconium oxides with a metallic copper additive are sufficiently strong (380 and 320 MPa, respectively, at a firing temperature of 1550°C).

Metal ceramics with ultradisperse copper additives can be used as an antifriction material. Copper powder that is industrially produced has weak adhesion to aluminum oxide. Moreover, aluminum oxide and copper have significantly different sintering temperatures, and therefore it is difficult to obtain a ceramic-metal material with prevalence of aluminum oxide and a slight additive of copper based on industrial powder by using traditional sintering. The use of superfine energy-saturated copper powder makes it possible, due to the high diffusion activity of the latter, to obtain cermet with a uniform distribution of metal on the surface and inside the volume of aluminum oxide grains (USSR Inventor's Certif. No. 1733427). Copper in friction forms a dense plating layer which decreases the friction coefficient and improves the wear resistance of the loaded friction pairs. The specific wear of ceramics with 2% copper SFP and a friction coefficient of 0.08 – 0.09 does not exceed 2.1×10^{-6} g/h. The material was obtained by hot molding in graphite molds at a temperature of 1500°C.

Recently a new aspect of using superfine electroexplosive metallic powders as materials capable of reinforcing ceramics has been discovered. It concerns the process of synthesis in combustion of aluminum mixed with minerals [10]. The high-temperature oxidation regime and binding air nitrogen from the gas-vapor phase lead to the formation of mono- and polycrystals of aluminum oxide, oxynitride, and nitride. The crystals have an elongated needle or filament shape and virtually pierce the silicate matrix (Fig. 7). In this way the effect of self-reinforcement of material is achieved.

The process can be implemented as combustion of freely poured batch with subsequent molding and sintering or as

SHS producing a finished or an intermediate product. Powder with reinforced particles can be used as a reinforcing additive in usual batch materials, for instance in clay-talc mixture for producing cordierite. The use of such additives significantly lowers sintering shrinkage (up to zero shrinkage), makes it possible to obtain materials of diverse porosity, and increases the bending strength 1.5 – 2 times.

Thus, despite their rather high cost, the use of small quantities of electroexplosive powders as activators in synthesis and sintering is promising for decreasing energy and metal consumption in the production of ceramic and composite materials. It is obvious as well that their use opens new vast possibilities for designing materials with diverse properties for different destinations.

REFERENCES

1. R. A. Andrievskii, "Production and properties of nanocrystalline high-melting compounds," *Usp. Khim.*, **63**(5), 431 – 448 (1994).
2. I. D. Morokhov, L. I. Trusov, and V. I. Lapovok, *Physical Phenomena in Ultradisperse Media* [in Russian], Énergoatomizdat (1984).
3. A. I. Gusev and A. A. Rempel', *Nanocrystalline Materials* [in Russian], Fizmatlit, Moscow (2001).
4. B. S. Bal'dzhinimaev, "Structural and catalytic properties of energy-saturated ultradisperse materials," *Ross. Khim. Zh.*, **45**(3), 59 – 65 (2001).
5. E. I. Azarkevich, A. P. Il'in, D. V. Tikhonov, and G. V. Yablunovskii, "Electroexplosive synthesis of ultradisperse powders, alloys, and intermetallic compounds," *Fiz. Khim. Obrab. Mater.*, No. 4, 85 – 88 (1997).
6. A. P. Il'in, "On excessive energy of ultradisperse powders obtained by the wire-explosion method," *Fiz. Khim. Obrab. Mater.*, No. 3, 94 – 97 (1994).
7. M. M. Mench, K. K. Kuo, C. L. Yeh, and Y. C. Lu, "Comparison of thermal behavior of regular and ultrafine aluminum powders (alex) made from plasma explosion process," *Combust Sci. Techn.*, **135**, 292 (1998).
8. T. A. Khabas, "Energy-saturated ultradisperse metal powders in technology of ceramic materials," *Steklo Keram.*, No. 11, 27 – 30 (1997).
9. T. A. Khabas, A. P. Il'in, and L. A. Lukovskaya, "A study of characteristics of metal-oxide composites for soldering in the W – SiO₂ system," *Adgez. Raspl. Paika Mater.*, No. 22, 92 – 95 (1989).
10. T. A. Khabas, A. P. Il'in, V. I. Vereshchagin, and E. M. Popenko, "Synthesis of ceramic powders in combustion of aluminum with silicate materials," in: *Proc. All-Russia Conf. "Combustion and Explosion Processes in Physical Chemistry and Technology of Inorganic Materials,"* Moscow (2002), pp. 497 – 500.